SOLID POLYMER FUEL CELL
[Kotai kobunshigata nenryo denchi]

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[Claims]

[Claim 1] A solid polymer fuel cell comprising an anode electrode and a cathode electrode each consisting of a catalytic layer and a support layer, and an ion-exchange membrane with proton conductivity interposed between this anode electrode and cathode electrode, wherein

the most hydrophilic material outside of the ion-exchange membrane is contained in the cathode electrode.

[Claim 2] The solid polymer fuel cell of Claim 1, wherein the layer containing the hydrophilic material is arranged between the catalytic layer and the support layer of the cathode electrode.

[Claim 3] The solid polymer fuel cell of Claim 1 or Claim 2, wherein the hydrophilic material is a metal oxide, such as SiO_2, SnO_2 and Al_2O_3.

[Claim 4] The solid polymer fuel cell of Claim 2, wherein the layer containing the hydrophilic material arranged between the catalytic layer and the support layer is thinner than the catalytic layer and the support layer.

[Detailed Description of the Invention]

[0001] [Technical Field of the Invention]

The present invention relates to a solid polymer fuel cell using an ion-exchange membrane with proton conductivity as the electrolyte.

[0002] [Prior Art]

FIG 3 is a diagram showing the configuration of a solid polymer fuel cell of the prior art. This solid polymer fuel cell, as shown in

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FIG 3, uses an ion-exchange membrane 1 with proton conductivity as the electrolyte, and consists of this ion-exchange membrane 1 interposed between an anode electrode 2 and a cathode electrode 3.

[0003] Nafion (Dupont), Flemion (Asahi Glass), Aciplex (Asahi Kasei) or Dow (Dow Chemical) is commonly used in the ion-exchange membrane 1. The electrodes 2, 3 consist of a catalytic layer 4 and a support layer 5 for supporting the catalytic layer 4. The catalytic layers 4 of these electrodes are configured so as to come into contact with the ion-exchange membrane 1. Electricity is generated by supplying the fuel gas containing hydrogen to the anode electrode 2 and by supplying oxidant gas containing air to the cathode electrode 3.
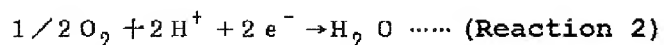
[0004] The hydrogen (H_2) contained in the fuel gas is oxidized by the anode electrode 2 in accordance with the following reaction.
[Formula 1]

$$H_2 \rightarrow 2H^+ + 2e^- \ \dots\dots \ (Reaction \ 1)$$

The H^+ (protons) travel through the ion-exchange membrane 1 while the e^- (electrons) perform electrical work via the external load 8. Both eventually reach the cathode electrode 3. The cathode electrode 3 reduces the oxygen (O_2) in the oxidant gas via a reaction with the H^+ and the e^-.
[Formula 2]

$$1/2\,O_2 + 2\,H^+ + 2\,e^- \rightarrow H_2O \ \dots\dots \ (Reaction \ 2)$$

The oxidation and reduction reactions continue and the fuel cell continues to generate electricity as long as the fuel gas and the

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oxidant gas are supplied. Because the output from a single fuel cell is so small, a solid polymer fuel cell usually consists of multiple layers divided by separators as shown in FIG 3. Thus, each fuel cell acts as a single fuel cell unit.

[0005] The ion-exchange membrane 1 manifests effective proton conductivity by including water. Therefore, the membrane has to contain water (i.e., be aqueous) in order for the solid polymer fuel cell to provide practical performance. However, the amount of water in the ion-exchange membrane 1 of a solid polymer fuel cell changes due to the following factors.

[0006] (1) The H^+ (protons) traveling from the anode electrode 2 to the cathode electrode 3 via the ion-exchange membrane 1 moves in accordance with the number of water molecules (H_2O).

(2) Water is generated at the cathode electrode 3 through the reduction of oxygen.

(3) Some of the water (H_2O) in (1) and (2) spreads from the cathode electrode 3 to the anode electrode 2.

(4) Some of the water is removed from the fuel cell via the anode electrode 2 side of the ion-exchange membrane 1 due to the fuel gas.

(5) Some of the water is removed from the fuel cell via the cathode electrode 3 side of the ion-exchange membrane 1 due to the oxidant gas.

[0007] Here, (1) and (2) depend on the reaction rate of the fuel cell and are a factor in the increase in the amount of water on the cathode electrode 3 side of the membrane. Because some of (3) is (1)

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and (2), the amount of water on the anode electrode 2 side of the membrane tends to decrease.

[0008] (4) and (5) are factors in the decrease in the amount of water in the membrane. While they also are factors in the increase in the amount of water, the flow rate in an actual fuel cell is greatly impacted by (4) and (5). The membrane dries out in a short period of time, and the characteristics of the fuel cell decrease. In order to offset this phenomenon, water has to be included beforehand in either the fuel gas or the fuel gas and the oxidant gas using any method common in the art. In other words, a means has to be provided for supplying moisturizing water to the ion-exchange membrane 1 via the electrodes.

[0009] Moisturizing the fuel gas can keep the ion-exchange membrane 1 from drying out on the anode side due to (1) and (4). The oxidant gas does not have to be moisturized, but the moisturizing of the oxidant gas can keep the ion-exchange membrane 1 from drying out on the cathode electrode 3 side if (1) + (2) < (5).

[0010] Moisturizing the reaction gases in this way can keep the ion-exchange membrane 1 from drying out but, because the moisturized reaction gases reach the ion-exchange membrane 1 via the electrodes, the configuration of the electrodes is also a factor having an impact on the characteristics of the solid polymer fuel cell.

[0011] The catalytic layer 4 is a layer containing a catalyst used to accelerate Reaction 1 and Reaction 2, respectively, in the anode electrode 2 and the cathode electrode 3. The catalyst is usually

platinum black, but fine particles of an alloy of platinum or an alloy of platinum and some other metal (i.e., a platinum alloy) with catalytic action can also be dispersed and supported on a carbon surface with a high specific surface area such as acetylene black or finesse black (carbon-supported platinum catalyst).

[0012] Thus carbon-supported platinum catalyst increases the specific surface area of the platinum thereby reducing the amount of platinum used. However, this arrangement is bulky because of the low-density carbon it contains, and the catalytic layer 4 has a porous structure reflecting the finely porous structure of the carbon.

[0013] This porous structure reduces the fuel cell properties in two ways. (a) The ratio of platinum or platinum alloy that cannot come into contact with the ion-exchange membrane 1 (i.e., cannot supply protons) is increased. This diminishes the catalytic activity in the fuel cell. (b) The water supplied to the membrane in the gases and the water generated by the fuel cell reaction remain in the pores, blocking the movement of the gas and reducing the distribution of gas in the fuel cell.

[0014] Problem (a) occurs because the solid ion-exchange membrane 1 cannot penetrate into the pores of the catalytic layer 4. As a result, a means is required to increase the utilization rate of the platinum and platinum alloy by mixing a dispersion solution of a polymer with the same composition as the ion-exchange membrane 1 with the catalyst to form the catalytic layer 4. Problem (b) is usually

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avoided by mixing fine particles with water repellent properties in the catalytic layer 4.

[0015] Examples of fine particles with water repellent properties include grinding a mixture of a fluorine resin such as Teflon (a tetrafluoroethylene resin manufactured by Dupont) and carbon to obtain carbon/fluorine resin particles, or fluorinating the surface of carbon or pitch to obtain fluorinated carbon or fluorinated pitch. Mixing these water repellent particles into the catalytic layer 4 makes the supply of water to the membrane and the removal of water generated by the fuel cell reaction go more smoothly.

[0016] The catalytic layer 4 is thin (< 200 μm) and fragile. Because the membrane is also relatively soft, it is often difficult to handle as a layer. As a result, a support layer 5 is used to reinforce these layers. The functions required of a support layer 5 are ease of use in a fuel cell, strength to withstand lamination, electric conductivity, and gas diffusion. A carbon material with a porous structure usually has to be treated for water repellency.

[0017] Specifically, carbon paper such as TGP (Toray) can be rendered water repellent by a fluorine resin, or a mixture of carbon and a fluorine resin can be baked and solidified in the form of a sheet. Because both of these methods contain a fluorine resin, water is kept from becoming trapped in the fine pores of the catalytic layer 4 as in the case of problem (b).

[0018] In this situation, only the catalytic layer 4 shown in FIG 3 is truly an electrode and the support layer 5 is treated separately.

However, the configuration of the electrodes and support layer in a fuel cell unit has the same configuration as the catalytic layer 4 and the support layer 5 in FIG 3, then a fuel cell unit here is a fuel cell of the prior art in all but name.

[0019] [Problem Solved by the Invention]

In a solid polymer fuel cell of the prior art with this configuration, the ion-exchange membrane 1 has to be supplied with water via moisturized reaction gases in order to keep the water content high. However, the water in the reaction gases cannot be retained in the electrodes. In other words, in this configuration, water is readily supplied to the electrodes but the water just as readily leaves. The supplied water also includes the water generated in the fuel cell reaction. Nearly all of this water is discharged from the fuel cell via the unreacted fuel gas and oxidant gas. In other words, a large amount of water is discharged from the fuel cell. Of course, the discharged water can be recycled and resupplied to the fuel cell. However, in this case, a large amount of water has to be stored in the fuel cell plant. This does not, in other words, solve the problem.

[0020] In light of this situation, the purpose of the present invention is to provide a solid polymer fuel cell that reduces the amount of water discharged from the fuel cell while using the same amount of water in the ion-exchange membrane as the prior art and without reducing the fuel cell properties.

[0021] [Means of Solving the Problem]

In order to solve this problem, the invention in claim 1 is a solid polymer fuel cell comprising an anode electrode and a cathode electrode each consisting of a catalytic layer and a support layer, and an ion-exchange membrane with proton conductivity interposed between this anode electrode and cathode electrode, wherein the most hydrophilic material outside of the ion-exchange membrane is contained in the cathode electrode.

[0022] The invention in claim 2 is the solid polymer fuel cell of claim 1, wherein the layer containing the hydrophilic material is arranged between the catalytic layer and the support layer of the cathode electrode.

[0023] The invention in claim 3 is the solid polymer fuel cell of claim 1 or claim 2, wherein the hydrophilic material is a metal oxide such as SiO_2, SnO_2 and Al_2O_3.

[0024] The invention in claim 4 is the solid polymer fuel cell of claim 2, wherein the layer containing the hydrophilic material arranged between the catalytic layer and the support layer is thinner than the catalytic layer and the support layer.

[0025] [Embodiment of the Invention]

The following is an explanation of an embodiment of the present invention with reference to the drawings.

[0026] FIG 1 is a simplified diagram of the solid polymer fuel cell in an embodiment of the present invention. The components

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identical to those in the prior art are denoted by the same numbers as those in FIG 3.

[0027] As shown in FIG 1, the solid polymer fuel cell in this embodiment uses an ion-exchange membrane 1 with proton conductivity as the electrolyte, and this ion exchange membrane 1 is interposed between an anode electrode 2 and a cathode electrode 3. These electrodes 2, 3 both consist of a catalytic layer 4 and a support layer 5 for supporting this catalytic layer 4. The two catalytic layers 4 are configured so as to come into contact with the ion-exchange membrane 1.

[0028] Here, the cathode electrode 3 contains the most hydrophilic material outside of the ion-exchange membrane 1. More specifically, a hydrophilic layer 6 containing a hydrophilic material and thinner than both the catalytic layer 4 and the support layer 5 is formed between the catalytic layer 4 and the support layer 5. Here, the hydrophilic material is a metal oxide such as SiO_2, SnO_2 or Al_2O_3.

[0029] A fuel cell unit with this configuration is incorporated into the fuel cell jig 7. Fuel gas containing moisturized hydrogen is supplied from the fuel gas inlet 7a to the anode electrode 2, and an oxidant gas containing moisturized air is supplied from the oxidant gas inlet 7c to the cathode electrode 3 in order to generated electricity. The fuel gas and the oxidant gas are discharged, respectively, from the fuel gas outlet 7b and the oxidant gas outlet 7d.

[0030] The following is a more detailed explanation of the solid polymer fuel cell in this embodiment.

[0031] First, 300 μm-thick carbon paper is permeated with a tetrafluoroethylene resin dispersion and heat-treated in a furnace at 350°C for 20 minutes to obtain the support layer 5. Next, carbon and Al_2O_3 metal oxide powder are mixed with an alcohol solvent at a 6:4 ratio to synthesize an ink, which is applied to the support layer 5 and dried to form a hydrophilic layer 6.

[0032] Next, a carbon-supported platinum catalyst and 5% Nafion solution are mixed at a 1:3 ratio to synthesize an ink, which is applied to the hydrophilic layer 6 and dried to form a catalytic layer 4 and complete the cathode electrode 3. The anode electrode 2 is manufactured in the same way except that a hydrophilic layer 6 is not formed. Instead, the catalytic layer 4 is formed directly on top of the support layer 5. The thickness of the catalytic layer 4 in both the anode electrode 2 and the cathode electrode 3 is approximately 100 μm. A Nafion membrane is used as the ion-exchange membrane 1, and the anode electrode 2 and the cathode electrode 3 are pressed against the Nafion membrane to complete the fuel cell unit. At this time, the amount of ink applied in the hydrophilic layer 6 is adjusted so that two other types of fuel cell unit are created, one with a 50 μm-thick hydrophilic layer 6 and one with a 150 μm-thick layer. Except for the hydrophilic layer 6 formed in the cathode electrode 3, the configuration is the same as a fuel cell of the prior art.

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[0033] These three types of fuel cell unit are incorporated into a fuel cell jig 7, and moisturized hydrogen is supplied from the fuel gas inlet 7a and moisturized air is supplied from the oxidant gas inlet 7c to generate electricity. The amount of moisture in the hydrogen and air is adjusted to maximize the fuel cell properties. When electricity was generated for 100 hours, the amount of water discharged from the fuel gas outlet 7b and the oxidant gas outlet 7d during this period was measured. The amount of water from a fuel cell of the prior art was approximately 650 mL. In contrast, the amount of water discharged from the fuel cells with 50 μm-thick and 150 μm-thick hydrophilic layers 6 was approximately 300 mL and 200 mL, respectively. When the fuel cell resistance was measured, the difference in both fuel cells did not even change 3 mΩ.

[0034] The fuel cell properties after 100 hours of operation are shown in FIG 2. As shown FIG 2, the properties of the fuel cell with a 50 μm-thick hydrophilic layer were essentially the same as a fuel cell of the prior art, but the fuel cell with a 150 μm-thick hydrophilic layer had a lower voltage than the fuel cell of the prior art in the high current range. The results from fuel cells using SiO_2 and SnO_2 as the hydrophilic material were similar to a fuel cell using Al_2O_3.

[0035] The low properties of the fuel cell with the 150 mm-thick hydrophilic layer are believed to have been cause by the hydrophilic layer 6 retaining water and blocking the diffusion of air. While the hydrophilic layer 6 contributes to a reduction in the amount of water discharged, it becomes water repellent when the thickness of the

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catalytic layer 4 and the support layer 5 in the cathode electrode 3 is exceeded. The hydrophilic catalytic layer 4 and support layer 5 remain unchanged, and the water retention blocks the diffusion of the reaction gases. When the reverse is true, the diffusion of the reaction gases is not impaired by the catalytic layer 4 and the support layer 5 even when water is retained. The function of the hydrophilic layer 6 can also be augmented by hydrophilic treatment of both layers.

[0036] However, if a novel function such as hydrophilia is added to a catalytic layer 4 and support layer 5 with their original functions, it is difficult to adjust the amount of hydrophilia and the original functions of the catalytic layer 4 and the support layer 5 may be compromised. It is easier to form the hydrophilic layer 6 separately and adjust the composition and amount of material. This has the further advantage of not requiring a design change to existing electrodes.

[0037] The hydrophilic properties of the hydrophilic layer 6 in the embodiment are relative inside the fuel cell outside of the ion-exchange membrane 1. In other words, it is not the most hydrophobic layer outside of the ion-exchange membrane 1. Therefore, when the catalytic layer 5 and the support layer 5 are treated for water repellency using a fluorine resin, the hydrophilic layer 6 can simply be untreated carbon. This would have the same action as the hydrophilic layer 6 described above.

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[0038] In this embodiment, the most hydrophilic material outside of the ion-exchange membrane 1 was included in the cathode electrode 3. As a result, the water moving with the H^+ (protons) and the water generated by the fuel cell reaction were trapped by this hydrophilic material. This keeps the ion-exchange membrane 1 from drying out and reduced the amount of moisturizing water that is required.

[0039] By arranging a hydrophilic layer 6 containing a hydrophilic material between the catalytic layer 4 and a support layer 5, the water generated by the fuel cell reaction with the water accompanying the H+ (protons) is retained in a position near the ion-exchange membrane 1, and a reduction in the amount of water contained in the ion-exchange membrane 1 is strongly suppressed. Because the ion-exchange membrane 1 does not dry out and the flow of water to the support layer 5 is suppressed, water does not build up in the support layer 5 and the spread of reaction gas to the support layer 5 is not prevented.

[0040] Because the hydrophilic material is a metal oxide such as SiO_2, SnO_2 or Al_2O_3, the water generated by the fuel cell reaction with the water accompanying the H+ (protons) is captured by a metal oxide such as SiO_2, SnO_2 or Al_2O_3 and the ion-exchange membrane 1 is kept from drying out. This can reduce the amount of moistening water that is required.

[0041] Because the hydrophilic layer 6 containing the hydrophilic material arranged between the catalytic layer 4 and the support layer 5 is thinner than the catalytic layer 4 and the support layer 5, the

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spread of reaction gas is not prevented even when the hydrophilic layer 6 retains water.

[0042] [Effect of the Invention]

As explained above, the invention in Claim 1 is able to obtain a solid polymer fuel cell that reduces the amount of water discharged from the fuel cell while using the same amount of water in the ion-exchange membrane as the prior art and without reducing the fuel cell properties. This is done by including the most hydrophilic material outside of the ion-exchange membrane in the cathode electrode.

[0043] In Claim 2, a layer containing a hydrophilic material is installed between the catalytic layer and a support layer. As a result, the water generated by the fuel cell reaction with the water accompanying the H+ (protons) is retained in a position near the ion-exchange membrane, and a reduction in the amount of water contained in the ion-exchange membrane is strongly suppressed. Because the ion-exchange membrane does not dry out and the flow of water to the support layer is suppressed, water does not build up in the support layer and the spread of reaction gas to the support layer is not prevented.

[0044] In claim 3, the hydrophilic material is a metal oxide, such as SiO_2, SnO_2 or Al_2O_3. As a result, the water generated by the fuel cell reaction with the water accompanying the H+ (protons) is captured by a metal oxide such as SiO_2, SnO_2 or Al_2O_3 and the ion-exchange membrane is kept from drying out. This can reduce the amount of moistening water that is required.

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[0045] In Claim 4, the layer containing the hydrophilic material arranged between the catalytic layer and the support layer is thinner than the catalytic layer and the support layer. As a result, the spread of reaction gas is not prevented even when the hydrophilic layer retains water.

[Brief Explanation of the Figures]

[FIG 1] A simplified diagram of the solid polymer fuel cell in an embodiment of the present invention.

[FIG 2] A graph showing the relationship between the fuel cell characteristics of this embodiment and a fuel cell of the prior art.

[FIG 3] A diagram showing the configuration of a solid polymer fuel cell of the prior art.

[Key to the Figures]

1 ... Ion-Exchange Membrane

2 ... Anode Electrode

3 ... Cathode Electrode

4 ... Catalytic Layer

5 ... Support Layer

6 ... Hydrophilic Layer

7 ... Fuel Cell Jig
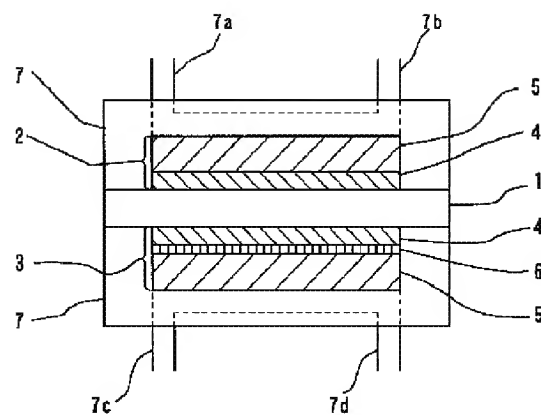
7a ... Fuel Gas Inlet
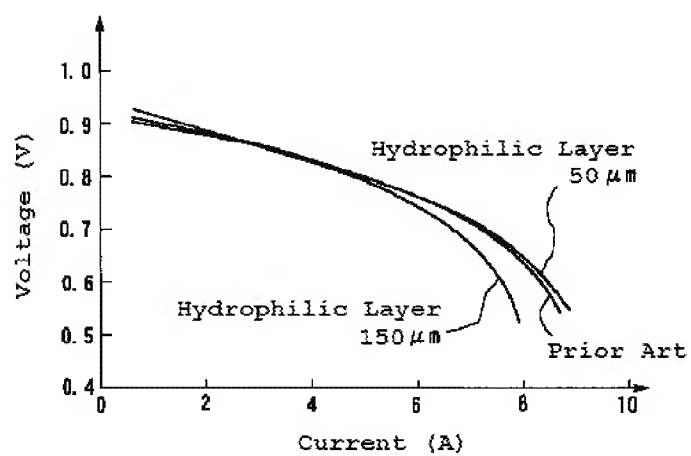
7b ... Fuel Gas Outlet

7c ... Oxidant Gas Inlet

7d ... Oxidant Gas Outlet

8 ... External Load

[FIG 1]

[FIG 2]

[FIG 3]

Fuel Gas + Water   Fuel Gas + Water

Oxidant Gas + Water   Oxidant Gas + Water